

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(guanidinium) chloranilate

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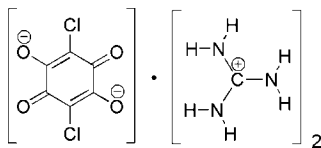
Received 10 August 2011; accepted 6 September 2011

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.078; data-to-parameter ratio = 14.4.

The asymmetric unit of the title co-crystal, $2\text{CH}_6\text{N}_3^+ \cdot \text{C}_6\text{Cl}_2\text{O}_4^{2-}$, contains one half of a chloranilate anion and one guanidinium cation, which are connected by strong $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds into a two-dimensional network.

Related literature

For organic co-crystals containing 2,5-dihydroxy-3,6-dichloro-1,4-benzoquinone (chloranilic acid), see: Andersen & Andersen (1975); Horiuchi *et al.* (2005, 2007); Zaman *et al.* (1999*a,b*, 2010). For inorganic co-ordination polymers containing chloranilic acid, see: Kitagawa *et al.* (2002). For guanidine and guanidinium structures, see: Abrahams *et al.* (2004, 2005); Best *et al.* (2003); Said *et al.* (2006); Smith & Wermuth (2010, 2011).



Experimental

Crystal data

$2\text{CH}_6\text{N}_3^+ \cdot \text{C}_6\text{Cl}_2\text{O}_4^{2-}$
 $M_r = 327.14$
 Monoclinic, $C2/c$
 $a = 19.5224$ (14) Å
 $b = 3.7316$ (3) Å
 $c = 18.4103$ (14) Å
 $\beta = 116.087$ (1)°

$V = 1204.56$ (16) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.57$ mm⁻¹
 $T = 173$ K
 $0.45 \times 0.40 \times 0.30$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
 Absorption correction: multi-scan (SADABS, Sheldrick, 1996)
 $T_{\min} = 0.785$, $T_{\max} = 0.849$
 6965 measured reflections
 1674 independent reflections
 1525 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.078$
 $S = 1.08$
 1674 reflections
 116 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|------------|--------------|--------------|----------------|
| $\text{N1}-\text{H2} \cdots \text{O3}$ | 0.85 (2) | 2.32 (2) | 3.0504 (13) | 144.4 (16) |
| $\text{N1}-\text{H1} \cdots \text{O2}^{\text{i}}$ | 0.901 (17) | 2.117 (17) | 2.8978 (13) | 144.4 (15) |
| $\text{N1}-\text{H1} \cdots \text{O3}^{\text{i}}$ | 0.901 (17) | 2.303 (18) | 3.0555 (13) | 140.9 (15) |
| $\text{N2}-\text{H3} \cdots \text{O3}$ | 0.818 (19) | 2.161 (19) | 2.9337 (14) | 157.7 (17) |
| $\text{N3}-\text{H6} \cdots \text{O2}^{\text{i}}$ | 0.79 (2) | 2.21 (2) | 2.9016 (14) | 146.3 (18) |
| $\text{N3}-\text{H5} \cdots \text{O2}^{\text{ii}}$ | 0.88 (2) | 2.14 (2) | 2.9586 (13) | 154.4 (17) |

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{5}{2}, -z$; (ii) $x, -y + 3, z - \frac{1}{2}$.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ATOMS (Dowty, 1999); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VM2118).

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supporting information

Acta Cryst. (2011). E67, o2625 [https://doi.org/10.1107/S1600536811036373]

Bis(guanidinium) chloranilate

Konstantin A. Udachin, Md. Badruz Zaman and John A. Ripmeester

S1. Comment

The co-crystallization of chloranilic acid and guanidine was carried out in methanol resulting in the co-crystal $2\text{CH}_6\text{N}_3^+ \cdot \text{C}_6\text{O}_4\text{Cl}_2^{2-}$ (Fig. 1). The chloranilic acid molecule is centro-symmetric and contains two hydrogen bond donors and two hydrogen bond acceptors and is, therefore, capable of participating in multiple hydrogen bonds. It forms 2D-sheet-like networks through N3—H5 \cdots O2 hydrogen bonds as shown in Figure 2. There are three N—H bonds in guanidine that connect with the O2 and O3 atoms of the chloranilic acid and form a one-dimensional molecular supramolecular structure. Two of these one-dimensional structures are again connected *via* N3—H5 \cdots O2 hydrogen bonds and form a two-dimensional network. Details of hydrogen-bonds are shown in Table 1.

S2. Experimental

Crystals were grown by slow evaporation of a methanol solution under ambient conditions containing a 1:1 stoichiometric quantity of guanidinium carbonate (Aldrich, 98%) and chloranilic acid (Aldrich, 99%).

S3. Refinement

Hydrogen atoms were found from the difference electron density maps and refined with isotropic temperature factors.

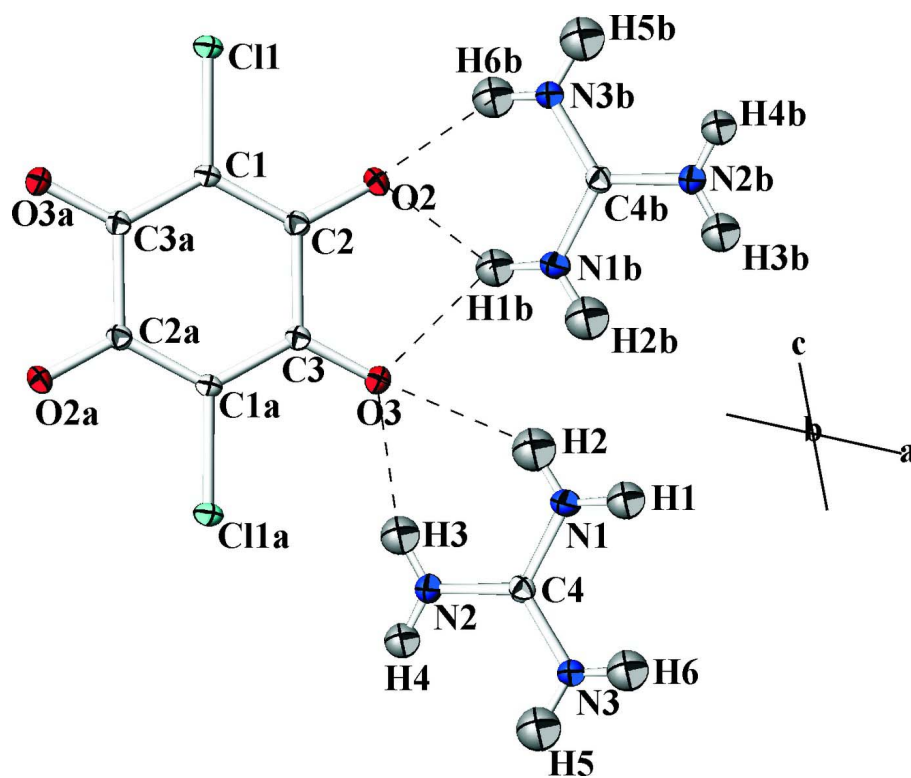


Figure 1

Molecular structure and atom naming scheme. Displacement ellipsoids are drawn at the 50% probability level. Grown fragment generated by symmetry codes: (a) $-x, 2-y, -z$; (b) $1/2-x, 2.5-y, -z$.

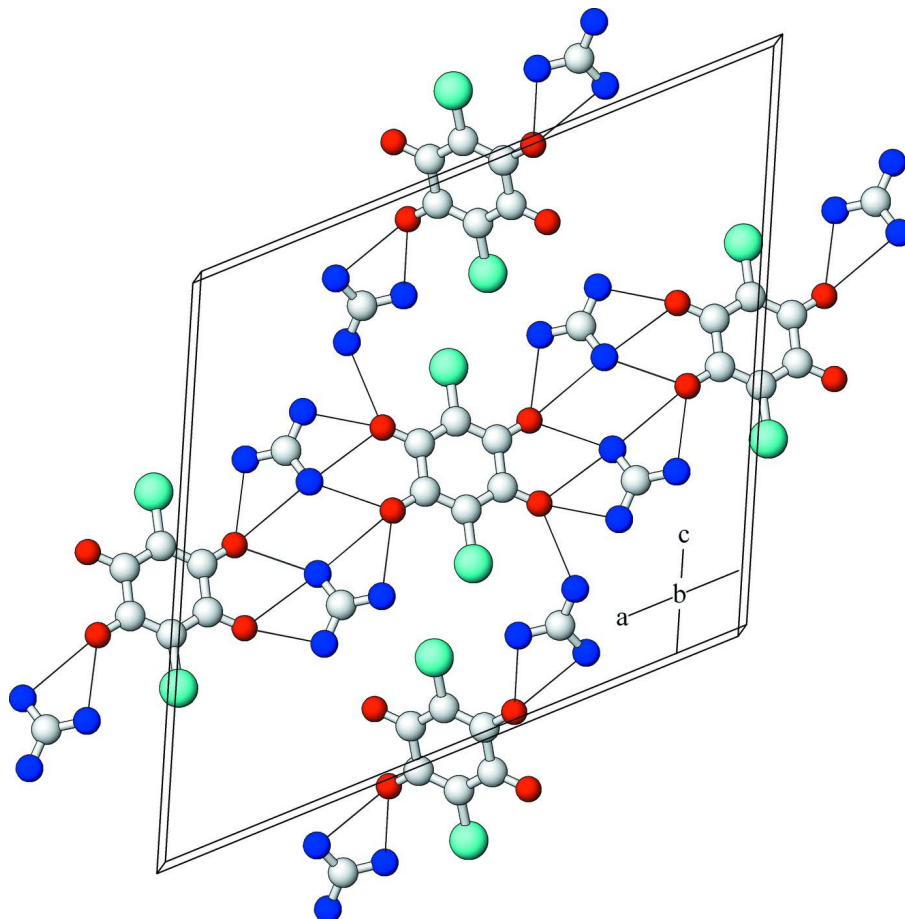


Figure 2

Packing diagram of the hydrogen-bonded framework structure of co-crystals viewed down the b axis, showing hydrogen-bonding associations as thin lines (H atoms are omitted).

Bis(guanidinium) 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate)

Crystal data

$2\text{CH}_6\text{N}_3^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}$

$M_r = 327.14$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 19.5224\ (14)\ \text{\AA}$

$b = 3.7316\ (3)\ \text{\AA}$

$c = 18.4103\ (14)\ \text{\AA}$

$\beta = 116.087\ (1)^\circ$

$V = 1204.56\ (16)\ \text{\AA}^3$

$Z = 4$

$F(000) = 672$

$D_x = 1.804\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71070\ \text{\AA}$

Cell parameters from 220 reflections

$\theta = 4.0\text{--}29.0^\circ$

$\mu = 0.57\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Block, yellow

$0.45 \times 0.40 \times 0.30\ \text{mm}$

Data collection

Bruker SMART 1000 CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*, Sheldrick, 1996)

$T_{\min} = 0.785$, $T_{\max} = 0.849$

6965 measured reflections

1674 independent reflections

1525 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 29.6^\circ$, $\theta_{\text{min}} = 2.3^\circ$

$h = -27 \rightarrow 27$
 $k = -5 \rightarrow 5$
 $l = -25 \rightarrow 25$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.078$
 $S = 1.08$
 1674 reflections
 116 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.7637P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.25 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|-------------|---------------|----------------------------------|
| C11 | 0.036370 (14) | 0.71393 (8) | 0.174949 (15) | 0.01677 (10) |
| O2 | 0.14122 (4) | 1.0852 (3) | 0.12281 (5) | 0.01823 (18) |
| O3 | 0.11119 (5) | 1.3347 (3) | -0.02492 (5) | 0.01949 (19) |
| N1 | 0.23429 (6) | 1.5093 (3) | -0.07912 (6) | 0.0213 (2) |
| H2 | 0.2183 (11) | 1.461 (6) | -0.0438 (12) | 0.037 (5)* |
| H1 | 0.2810 (10) | 1.436 (5) | -0.0711 (10) | 0.028 (4)* |
| N2 | 0.11581 (6) | 1.7324 (3) | -0.16016 (7) | 0.0201 (2) |
| H4 | 0.0871 (10) | 1.852 (5) | -0.1996 (11) | 0.024 (4)* |
| H3 | 0.1026 (10) | 1.648 (5) | -0.1273 (11) | 0.030 (5)* |
| N3 | 0.21154 (6) | 1.7664 (3) | -0.20145 (7) | 0.0211 (2) |
| H6 | 0.2549 (12) | 1.736 (5) | -0.1912 (12) | 0.034 (5)* |
| H5 | 0.1782 (11) | 1.824 (6) | -0.2505 (13) | 0.039 (5)* |
| C1 | 0.01581 (6) | 0.8726 (3) | 0.07862 (6) | 0.0143 (2) |
| C2 | 0.07504 (6) | 1.0395 (3) | 0.06811 (6) | 0.0140 (2) |
| C3 | 0.05815 (6) | 1.1811 (3) | -0.01681 (6) | 0.0139 (2) |
| C4 | 0.18720 (6) | 1.6695 (3) | -0.14746 (7) | 0.0154 (2) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|-------------|
| C11 | 0.01745 (15) | 0.02061 (16) | 0.01101 (15) | -0.00081 (9) | 0.00514 (11) | 0.00188 (9) |
| O2 | 0.0120 (3) | 0.0267 (4) | 0.0132 (4) | -0.0009 (3) | 0.0030 (3) | 0.0000 (3) |

| | | | | | | |
|----|------------|------------|------------|-------------|------------|-------------|
| O3 | 0.0147 (4) | 0.0274 (5) | 0.0165 (4) | -0.0040 (3) | 0.0069 (3) | 0.0016 (3) |
| N1 | 0.0181 (5) | 0.0293 (5) | 0.0165 (5) | 0.0044 (4) | 0.0077 (4) | 0.0056 (4) |
| N2 | 0.0150 (4) | 0.0270 (5) | 0.0191 (5) | 0.0023 (4) | 0.0082 (4) | 0.0045 (4) |
| N3 | 0.0154 (5) | 0.0326 (6) | 0.0154 (5) | 0.0012 (4) | 0.0069 (4) | 0.0049 (4) |
| C1 | 0.0139 (4) | 0.0182 (5) | 0.0099 (4) | -0.0003 (4) | 0.0043 (4) | 0.0014 (4) |
| C2 | 0.0133 (4) | 0.0161 (5) | 0.0119 (4) | 0.0007 (4) | 0.0051 (4) | -0.0008 (4) |
| C3 | 0.0129 (5) | 0.0166 (5) | 0.0120 (5) | 0.0004 (4) | 0.0053 (4) | 0.0000 (4) |
| C4 | 0.0142 (5) | 0.0168 (5) | 0.0142 (5) | -0.0013 (4) | 0.0052 (4) | -0.0015 (4) |

Geometric parameters (Å, °)

| | | | |
|-----------------------|-------------|-------------------------|-------------|
| C11—C1 | 1.7409 (11) | N2—H3 | 0.818 (19) |
| O2—C2 | 1.2522 (13) | N3—C4 | 1.3267 (15) |
| O3—C3 | 1.2487 (13) | N3—H6 | 0.79 (2) |
| N1—C4 | 1.3297 (15) | N3—H5 | 0.88 (2) |
| N1—H2 | 0.85 (2) | C1—C2 | 1.3997 (14) |
| N1—H1 | 0.901 (17) | C1—C3 ⁱ | 1.4051 (14) |
| N2—C4 | 1.3287 (14) | C2—C3 | 1.5423 (15) |
| N2—H4 | 0.827 (18) | C3—C1 ⁱ | 1.4052 (14) |
| C4—N1—H2 | 118.9 (13) | C3 ⁱ —C1—C11 | 118.10 (8) |
| C4—N1—H1 | 121.3 (11) | O2—C2—C1 | 124.91 (10) |
| H2—N1—H1 | 119.6 (17) | O2—C2—C3 | 116.98 (9) |
| C4—N2—H4 | 120.2 (12) | C1—C2—C3 | 118.10 (9) |
| C4—N2—H3 | 116.7 (13) | O3—C3—C1 ⁱ | 125.41 (10) |
| H4—N2—H3 | 123.1 (17) | O3—C3—C2 | 117.36 (9) |
| C4—N3—H6 | 118.7 (14) | C1 ⁱ —C3—C2 | 117.23 (9) |
| C4—N3—H5 | 119.3 (13) | N3—C4—N2 | 120.90 (11) |
| H6—N3—H5 | 121.0 (18) | N3—C4—N1 | 120.33 (11) |
| C2—C1—C3 ⁱ | 124.66 (10) | N2—C4—N1 | 118.76 (11) |
| C2—C1—C11 | 117.24 (8) | | |

Symmetry code: (i) $-x, -y+2, -z$.*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H2 \cdots O3 | 0.85 (2) | 2.32 (2) | 3.0504 (13) | 144.4 (16) |
| N1—H1 \cdots O2 ⁱⁱ | 0.901 (17) | 2.117 (17) | 2.8978 (13) | 144.4 (15) |
| N1—H1 \cdots O3 ⁱⁱ | 0.901 (17) | 2.303 (18) | 3.0555 (13) | 140.9 (15) |
| N2—H3 \cdots O3 | 0.818 (19) | 2.161 (19) | 2.9337 (14) | 157.7 (17) |
| N3—H6 \cdots O2 ⁱⁱ | 0.79 (2) | 2.21 (2) | 2.9016 (14) | 146.3 (18) |
| N3—H5 \cdots O2 ⁱⁱⁱ | 0.88 (2) | 2.14 (2) | 2.9586 (13) | 154.4 (17) |

Symmetry codes: (ii) $-x+1/2, -y+5/2, -z$; (iii) $x, -y+3, z-1/2$.